

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



(21) International Application Number: PCT/US00/10824 (81) II (22) International Filing Date: 24 April 2000 (24.04.00) (30) Priority Data: 60/131,560 29 April 1999 (29.04.99) US 09/468,958 22 December 1999 (22.12.99) US (71) Applicant (for all designated States except US): IMERYS PIGMENTS, INC. [US/US]; 100 Mansell Court East, Suite 300, Roswell, GA 30076 (US).	BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF)		
(22) International Filing Date: 24 April 2000 (24.04.00) (30) Priority Data: 60/131,560 29 April 1999 (29.04.99) US 09/468,958 22 December 1999 (22.12.99) US (71) Applicant (for all designated States except US): IMERYS PIGMENTS, INC. [US/US]; 100 Mansell Court East, Suite 300, Roswell, GA 30076 (US).	BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasia patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), Europea patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF)		
 (72) Inventors; and (75) Inventors/Applicants (for US only): LYONS, Anthony, V. [US/US]; 140 Saddle Run Ct., Macon, GA 31210 (US). ZHANG, Zhichao, R. [-/US]; 342 Log Cabin Road, Apt. 10G, Milledgeville, GA 31061 (US). (74) Agents: GARRETT, Arthur, S. et al.; Finnegan, Henderson, Farabow, Garrett & Dunner, L.L.P., 1300 I Street, N.W., Washington, DC 20005-3315 (US). 	BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report.		
(54) Title: PIGMENT COMPOSITION FOR PAPER COATING,	olid bleached sulfite product to give a combination of improvorganic materials namely (a) a high brightness ultrafine kao size less than about 0.5 microns (μm); and (b) a fine coatigonite or rhombohedral crystal form, having a median parti-		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
ВЈ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	ŲZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
СН	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KР	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

-1-

TITLE OF THE INVENTION

PIGMENT COMPOSITION FOR PAPER COATING, PAPER COATING USING THE SAME AND METHOD OF COATING PAPER

5

This application claims the benefit of U.S. Patent Application No. 09/468,958, filed December 22, 1999, and U.S. Provisional Application No. 60/131,560, filed April 29, 1999.

10 BACKGROUND TO INVENTION

1. Field of the Invention

The present invention relates to a pigment composition for use in paper coating, a paper coating composition containing the same and a method of coating 15 paper using the same.

The properties of coated paper products, including paper sheet, packaging and board products, depend heavily on the formulation of the coating applied to the paper, especially the pigments employed in the coating 20 formulation. For some products, eg coated freesheet paper and coated solid bleached sulfite (SBS) board, sheet brightness is the most significant optical property required by manufacturers and users although other optical properties such as sheet gloss may also be 25 important to a lesser extent. In order to produce high sheet brightness in such products manufacturers, especially in North America, have previously used blends of fine kaolin with fine calcium carbonate in compositions for use in coating such paper products. The 30 main purpose of the present invention is to provide a

novel pigment composition of this kind giving an improved combination of coating properties.

2. Summary of the prior art

In the prior art, pigment blends of kaolin and 5 calcium carbonate for use in coating compositions have conventionally been prepared from ground calcium carbonate and kaolin typically with a high kaolin content in the blend. The level of calcium carbonate employed in such blends has in many cases been less than 50% of the 10 pigment weight. However methods have been sought to improve the coated sheet brightness of paper product sheets coated with compositions containing such pigment blends.

Although optical brightening agents (OBA's) may be 15 used to give an increase in observed sheet brightness from kaolin-containing coatings use of such agents is desirably avoided in many materials, especially those designed for packaging applications, since such agents generally are not approved by regulatory authorities such 20 as the US Food and Drugs Administration (FDA).

It has been found in a number of instances to be desirable to use a higher calcium carbonate content in kaolin/carbonate blends since calcium carbonate can be produced more cheaply than kaolin and has a greater 25 powder brightness than kaolin and this can provide a greater contribution to sheet brightness. In some previously used formulations attempts have therefore been made to employ higher carbonate contents in kaolin/calcium carbonate blends. However it has been

found that these previously used formulations are unsatisfactory as the resulting sheet gloss is lower than is desirable. In order to improve the sheet gloss for a given kaolin/carbonate blend, conventionally the level of scarbonate in the blend has to be reduced, which accordingly reduces the brightness of the coated paper or else high calendering pressure is required during the finishing stage which brings with it a cost penalty.

Plastic pigments may be used to avoid reducing the 10 gloss without a reduction in the calcium carbonate level or an increase in the calendering pressure. However, these pigments are costly and their use also causes an increase in the cost of the coating formulation.

The present invention aims to produce a novel
15 carbonate-rich pigment composition of calcium carbonate
and kaolin which does not cause a significantly reduced
gloss when used in a coating formulation to provide a
coating on a paper product, thereby advantageously
reducing the need to employ plastic pigments or high
20 calendering pressures and therefore bringing with it
significant economic benefits.

Another important property of the coating formulation is binder demand. Packaging products in particular have a high binder demand and it is desirable 25 to take steps to reduce this wherever possible in order to reduce the cost of the coated product. The binder demand is determined by the pigment specific surface area. The binder demand is lower for pigments of lower specific surface area.

Thus, the objects of the invention are to produce a pigment composition useful for coating paper and board products, especially packaging products, giving an improved combination of sheet brightness and sheet gloss and which may also have reduced coating binder demand. These and other objects which will become apparent hereinafter are fulfilled by the present invention.

US Patent No. 5833747 describes blends of aragonite PCC and platey kaolin. The present invention employs a 10 composition comprising a blocky rather than a platey kaolin which together with a PCC, both of selected median particle size in a selected carbonate-rich formulation, produces a sheet brightness and gloss which are both considerably higher than those reported in this prior art 15 patent.

SUMMARY OF THE PRESENT INVENTION

The present invention aims to produce a pigment composition for use in a coating composition for coating paper products which produces a coating structure on the 20 paper product that yields an improved combination of brightness and gloss and in some cases printability.

According to the present invention in a first aspect there is provided a pigment composition for use in coating a paper product, comprising a blend of at least 25 two particulate inorganic materials comprising (a) a high brightness ultrafine kaolin produced from a blocky kaolin clay the kaolin having a median particle size less than about 0.5 microns (um) and (b) a fine coating precipitated calcium carbonate (PCC) having a median 30 particle size less than about 0.8 microns, the ratio by

weight of the PCC to the kaolin being greater than 1.0. The PCC may have a selected crystal morphology, for example a predominantly aragonite or rhombohedral morphology.

According to the present invention in a second aspect there is provided a coating composition comprising an aqueous suspension comprising the pigment composition of the first aspect and a water borne binder.

According to the present invention in a third aspect 10 there is provided a method for coating a paper product by applying the coating composition of the second aspect to coat a surface of the paper product.

According to the present invention in a fourth aspect there is provided a method of improving the 15 optical and printing properties of a paper product, comprising applying the coating composition of the second aspect to at least one surface of said paper product.

For the purposes of the present invention the term 'paper product' includes paper sheets, paper packaging 20 and board products and the like. The paper product to be coated according to the present invention may be uncoated or it may carry one or more previously applied coating layers.

DESCRIPTION OF THE PRESENT INVENTION

25 Surprisingly, it has been found that by combining the high brightness ultrafine kaolin (a) with the PCC (b) which may be predominantly of a selected morphology, in the compositions of the invention both the sheet brightness and sheet gloss of resulting coated paper 30 products may be surprisingly and beneficially boosted to

-6-

a combined extent not obtained in the prior art for carbonate-rich calcium carbonate/kaolin blends

The composition according to the first aspect has a weight ratio of PCC to kaolin of greater than 1:1, 5 preferably from 5:4 to 10:1, especially 3:2 to 4:1.

The kaolin and the PCC in the composition of the invention both have a small specified median particle size. The median particle size of an inorganic pariculate material is the particle equivalent spherical 10 diameter ("esd") value less than which 50% of the particles have an esd. This is also referred to as the d_{50} value and may be measured in the manner described later.

The kaolin may beneficially have a median particle 15 size of less than about 0.3 microns, especially between about 0.10 microns and about 0.25 microns, eg between 0.15 microns and 0.25 microns, eg about 0.2 microns.

The PCC has a median particle size of less than about 0.8 microns, and this may be between about 0.2 and 20 about 0.7 microns, eg between about 0.25 microns and about 0.45 microns.

We have found, for example, that carbonate-rich blends of fine kaolin and fine aragonite or rhombohedral PCC unexpectedly produce favorable combinations of coated 25 sheet brightness and gloss.

The kaolin employed in the present invention may comprise in addition to kaolinite as a major component one or more minor impurity minerals, eg clay minerals of the smectite group which comprises bentonite, 30 montmorillonite, hectorite, beidellite and saponite or of

-7-

the kandite group, which comprises dicktite, nacrite and halloysite as well as kaolinite. Kaolinite containing minerals include china clays, kaolin type clays, ball clays and fire clays. For the purposes of the present 5 invention, a kaolin clay is defined as a clay containing at least 90% by weight, preferably at least 95% by weight kaolinite.

The kaolin employed in the present invention may have been treated by one or more processes which are well 10 known to those skilled in the art, for example by known refining or benefication steps. For example the kaolin clay may be bleached with a reductive bleaching agent, such as sodium hydrosulfite.

Without wishing to be bound by any particular theory
15 we believe that the high performance characteristics of
the pigment composition according to the first aspect of
the invention are a result of the high pore volume that
may be generated in the coating because of the unique
particle size and shape of the pigments associated with
20 both the kaolin (a) and the PCC (b). The large pore
volume and radius are responsible for efficient light
scattering which in turn provides high coating sheet
brightness. The blend of fine pigments beneficially
creates a microscopically smooth surface which
25 significantly improves the sheet gloss.

The kaolin in the compositions of the present invention may be a fine glossing kaolin, e.g. it may be a kaolin which when used as a coating pigment may produce a smooth surface on a coated paper product, eg it may have 30 a high proportion of fine particles, eg it may have

greater than 50%, e.g. greater than 60%, by weight of its particles having an esd less than 0.25 microns.

The unusual particle size properties of the kaolin and PCC as employed in the composition according to the first aspect may be illustrated by the particle size distribution ("psd") of these pigments. In this specification all pigment psd and median particle size measurements are as measured in a well known manner by sedimentation of the pigment in a fully dispersed 10 condition in an aqueous medium using a SEDIGRAPH 5100 machine as supplied by Micromeritics Corporation. Such a machine provides measurements and a plot of the cumulative percentage by weight of particles having an esd less than given esd values.

The kaolin employed in the pigment composition of the present invention may have in the fully dispersed state a particle size distribution such that the percentage P by weight of particles having a size less than xµm, where x is respectively 2µm, 1µm, 0.5µm and 200.25µm is as follows:

•	x (μm)	P (%)
-	2	at least 95
25	1	at least 93
	0.5	at least 85
	0.25	at least 50

In particular, the kaolin employed in the composition of 30 the present invention may have the particle size distribution as follows:

	X (um)	P (%)
	2	at least 99
	1	at least 98
	0.5	at least 93
5	0.25	at least 68

WO 00/66509

The median particle size may be measured by such an analysis and for the fine kaolin employed in the composition of the invention may be less than 0.2 10 microns, e.g. between 0.10 and 0.19 microns.

The PCC employed in the present invention may, if predominantly aragonite, have in the fully dispersed state a particle size distribution such that the percentage P by weight of particles having a size less 15 than xµm, where x is respectively 2µm, 1µm, 0.5µm and 0.25µm is as follows:

	x (μm)	P (%)
20	2	At least 92
	1	At least 75
	0.5	At least 60
	0.25	Between 15 and 40

25 e.g. the PCC employed in the present invention may have the particle size distribution as follows:

•	x (μm)	P (%)
•	2	at least 95
30	1	at least 82
	0.5	at least 66
	0.25	between 23 and 33

Alternatively, the PCC employed in the compositions of the present invention may, if predominantly rhombohedral, have in the fully dispersed state a particle size distribution such that the percentage P by 5 weight of particles having a size less than xµm, where x is respectively 2µm, 1µm, 0.5µm and 0.25µm, is as follows:

10

_	X (μm)	P (%)
_	2	at least 93
	1	at least 86
	0.5	at least 22
15	0.25	Between 5 and 25

e.g. the PCC employed in the compositions of the present invention may have the particle size distribution as follows (x and P as defined above):

20

_	x (μm)	P (%)
_	2	at least 97
	1	at least 90
	0.5	at least 25
25	0.25	between 7 and 17

The median particle size of such a rhombohedral PCC may be from about 0.4 to about 0.6 microns.

The kaolin employed in the compositions of the 30 present invention may be a kaolin having a high brightness, eg a GE powder brightness of at least 85, e.g. at least 90.

The PCC employed in the compositions of the invention may have a GE powder brightness of at least 90, e.g. at least 92.

The kaolin employed in the compositions of the 5 present invention may be obtained from a relatively blocky kaolin clay, eg obtained from a secondary kaolin deposit such as from South East USA, e.g. from Georgia. Such kaolin clays usually have a relatively low shape factor. "Shape factor" as used herein is a measure of an 10 average value (on a weight basis) of the ratio of mean particle diameter to mean particle thickness for a population of particles of varying size and shape as measured using the electrical conductivity method and apparatus described in GB-A-2240398/US-A-5128606/EP-A-15 0528078 and using the equations derived in these patent specifications. "Mean particle diameter" is defined as the diameter of a circle which has the same area as the largest face of the particle and is substantially the same as the median particle as defined earlier. The 20 shape factor of the kaolin employed in the composition of the invention may for example be less than 20, e.g. less than 15, eg less than 12, especially less than 10, eg less than 9, eg 8 or less. By employing a relatively blocky kaolin rather than a platey kaolin in the present 25 invention it is possible to produce runnable coating formulations or compositions having a higher solids concentration.

Calcium carbonates are known to precipitate in different crystal morphologies and the PCC used in the 30 compositions and method of the present invention may

WO 00/66509

-12-

PCT/US00/10824

comprise any one or more of these morphologies. PCC is known to exist in the aragonite (aragonitic) form in which the crystals are needle shaped or in the calcite (calcitic) form. Various sub-classes of these two forms for are referred to in the art. For example reference is often made to two main versions of the calcite form, namely rhombohedral in which the crystals have a rhomboid shape and scalenohedral in which the crystals have a kite shaped or double pyramid structure which favours twinning and growth of clusters. X-ray diffraction allows the aragonite and calcite forms to be distinguished and electron microscopy allows the rhombohedral and scalenohedral forms of the calcite form to be distinguished.

- The aragonite form crystallises as long, thin needles generally having a length:diameter ratio of about 10:1. The length to diameter ratio of the crystals of the selected form, if predominantly aragonite, may for example average at least 5:1.
- As is known to those familiar with the PCC art, the crystal form(s) obtained in the production of PCC depends upon a number of factors which have a complex relationship, such as the quantities and types of liquid, gaseous and solid species present, the temperature and, 25 where the source of carbonate ions comprises CO₂ gas, the gas application rate. The result is that it is common to produce together a mixture of different crystal forms. The PCC form achieved in practice is unlikely to be 100% of the selected form. It is quite usual for one PCC

30 crystal form even when predominant to be mixed with other

forms. Such mixed forms can give suitably improved product properties. We prefer that the PCC is produced by a controlled process providing that at least 50% by weight, desirably at least 75% by weight of the crystals in the PCC to be employed in the pigment composition of the present invention are of a selected crystal morphology.

The PCC employed by the present invention may therefore be predominantly of an aragonite morphology.

10 For example, at least 50%, e.g. at least 75%, of the PCC may be of the aragonite crystal form.

The PCC employed by the present invention may alternatively be predominantly of a rhombohedral morphology, For example, at least 50%, e.g. at least 75%, 15 may be of the rhombohedral crystal form.

The process conditions during the precipitation process required generally to achieve principally a selected PCC crystal morphology, eg an aragonitic or rhombohedral morphology, and a selected median particle 20 size, are known to those skilled in the art and are described for example in the literature, e.g. in ----

The pigment composition according to the first aspect of the present invention may be added to additional pigments, e.g. any of those known in the art 25 for use in coating applications. The blend of kaolin (a) and PCC (b) defined earlier may constitute 90% or more, in some cases 100% of the pigments present in the composition.

The pigment composition of the invention may be 30 formed by blending dry kaolin and dry PCC or it may be

formed using an aqueous suspension of one or both of the kaolin and the PCC.

The binder employed in the coating composition according to the second aspect of the present invention, 5 defined earlier, may comprise one or more binders or adhesives known and/or used in the paper product coating art, for example it may comprise a waterborne binder such as selected from (i) waterborne natural and synthetic polymeric latices; (ii) polysaccharides such as starch 10 and starch derivatives, and (iii) proteinaceous materials.

Where a latex is employed, the latex may comprise for example a styrene butadiene, acrylic latex, vinyl acetate latex, or a styrene acrylic copolymers. Where a 15 starch is employed, the starch may comprise material derived from maize, corn or potato.

Examples of other suitable binders or binder components include casein and polyvinyl alcohol.

The binder may be used, on an active basis, in an 20 amount of from 0.1% to 30% by weight, eg from 1% to 25%, especially from 4% to 20%, e.g. from 10% to 18%, based on the dry weight of the inorganic material, principally pigments, present. The synergy between the kaolin and PCC of the present invention allows for a reduced binder 25 demand compared to comparable prior art pigment compositions as illustrated later.

The binder may mainly or wholly of latex type (i) above. Optionally, a quantity of binder type (ii) or (iii) may be included together with type (i). For 30 example, the type (iii) binder may, together with type

-15-

(i) binder, optionally be used, on an active basis, in an amount of up to 10% by weight, eg from 0% to 5%, especially from 0 to 3%, eg from 1% to 2%, based on the dry weight of the pigment material.

The coating composition according to the second aspect of the invention thus contains as principal ingredients water, binder and the pigment composition of the invention (in its first aspect). The amount of water present is a suitable amount required to make the 10 composition fluid and runnable. Such an amount will depend on the nature of the other generally solid ingredients present, but will generally be between 20% and 40% by weight of the composition. Other ingredients in minor amounts, e.g. in total less than 5% by weight 15 may be incorporated in the coating composition to improve the properties of the composition. These additional ingredients and the typical quantities required are well known by those skilled in the paper coating art. The additional ingredients may include, for example, one or 20 more of pigment dispersant (dispersing agent) and lubricity/calendering aid, e.g. solid lubricant, eg calcium stearate.

The dispersant optionally employed in the composition according to the second aspect of the present 25 invention may be selected from any well known in the art, for example it may be a polyelectrolyte, eg a polyacrylate dispersant, e.g. sodium polyacrylate. The dispersant may be present, on an active basis, in an amount of from 0.01% to 1% by weight, e.g. from 0.05% to

0.5% by weight, based on the dry weight of the pigments present.

A solid lubricant may also optionally be added to the coating formulation, on an active basis, in an amount 5 of up to 3% by weight, e.g. from 0.1% to 1% by weight, based on the dry weight of pigments.

Further additional ingredients which may optionally be employed in the coating composition include optical brightening agents (OBA's), activators, cross linkers, 10 water retention aids, viscosity modifiers or thickeners, antifoamers/defoamers, dry or wet pick improvement additives, dry or wet rub improvement and abrasion resistance additives, gloss-ink hold-out additives, fluorescent whitening agents (FWA), dyes, 15 biocides/spoilage control agents, levelling and evening

15 biocides/spoilage control agents, levelling and evening aids, grease and oil resistance additives, water resistance additives and insolubilizer and these may be added in amounts well known in the paper coating art.

The paper product to be coated in the method

20 according to the third aspect of the invention may be
chosen from any of the paper products well known by those
skilled in the art as being suitable for coating by
binder and pigment containing aqueous compositions. Such
products will comprise on the surface to be coated or

25 in an underlying base sheet or structure a mixture of
cellulose fibres usually plus particulate fillers. The
paper product may for example be a paper sheet or a
packaging or board product, especially a freesheet or a
solid bleached sulfite paper product.

WO 00/66509

PCT/US00/10824

The paper products which are coated using the method according to the third aspect of the present invention may be uncoated or they may carry one or more previously applied coating layers. The previously applied layer(s) 5 may or may not be the same as that applied in the method.

Methods of coating paper and other sheet materials are widely published and well known. For example, there is a review of such methods published in Pulp and Paper 10 International, May 1994, page 18 et seq. Sheets may be coated on the sheet forming machine, ie "on-machine", or "off-machine" on a coater or coating machine. Use of high solids compositions is desirable in the coating method because it leaves less water to evaporate 15 subsequently. However, as is well known in the art, the solids level should not be so high that high viscosity and levelling problems are introduced.

All known methods of coating for use in coating paper using the coating formulation according to the 20 third aspect of the present invention require (I) a means of applying the coating formulation to the material to be coated, viz. an applicator; and (II) a means for ensuring that a correct level of coating formulation is applied, viz. a metering device. When an excess of coating 25 formulation is applied to the applicator, the metering device is downstream of it. Alternatively, the correct amount of coating formulation may be applied to the applicator by the metering device, eg as a film press. At the points of coating application and metering, the 30 paper web support ranges from a backing roll, eg via one

PCT/US00/10824

or two applicators, to nothing (ie just tension). The time the coating is in contact with the paper before the excess is finally removed is the dwell time - and this may be short, long or variable.

- The coating is usually added by a coating head at a coating station. According to the quality desired, paper grades are uncoated, single coated, double coated and even triple coated. When providing more than one coat, the initial coat (precoat) may have a cheaper
- 10 formulation. A coater that is applying a double coating, ie a coating on each side of the paper, will have two or four coating heads, depending on the number of sides coated by each head. Most coating heads coat only one side at a time, but some roll coaters (eg film press, 15 gate roll, size press) coat both sides in one pass.

Examples of known coaters which may be employed in coating of a sheet material using a composition according to the second aspect of the invention include air knife coaters, blade coaters, rod coaters, bar coaters, multi-20 head coaters, roll coaters, roll/blade coaters, cast coaters, laboratory coaters, gravure coaters, kiss coaters, liquid application systems, reverse roll coaters and extrusion coaters.

The coated paper product prepared by the method of 25 the third aspect of the present invention may have a brightness of at least 75 units, eg from 75 to 95 ISO units, e.g. at least 81 ISO units.

The coated paper product prepared by the method of the third aspect of the present invention may have a 30 sheet gloss, measured according to the TAPPI standard 75 degree gloss method, of at least 60 units, e.g. at least 65 units, e.g. from 65 to 75 units.

The coated paper product prepared by the method of the fourth aspect of the present invention may have a 5 print gloss, measured according to the TAPPI 75 degree gloss method using black offset ink and a standard print density of 1.6, of at least 85 units, eg from 93 to 99 units.

The coating of the coated paper product prepared by 10 the method of the second aspect of the present invention may have a pore volume of at least 5cm⁻³.kg⁻¹, eg from 5 to 15cm⁻³kq⁻¹.

The coating of the coated paper product prepared according to the method of the third aspect of the 15 present invention may have an average pore radius of at least 30nm, eg from 30 to 45nm, eg at least 35nm.

The coating of the coated paper product prepared according to the method of the third aspect of the present invention may have a surface micro roughness 20 measured (in the manner described later) using an atomic force microscope of less than $0.100\mu m,~e.g.$ from $0.050\mu m$ to $0.085\mu m$. The fine pigments of the composition according to the first aspect of the invention create such a microscopically smooth surface on the coated paper 25 product which significantly improves the sheet gloss of the coating as well as the brightness thereof. DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS OF THE INVENTION.

Embodiments of the present invention will now be described by way of example with reference to the

WO 00/66509

-20-

following Examples which include, for comparison purposes, examples of prior art procedures.

EXAMPLE 1

A pigment composition embodying the invention was 5 prepared using an ultrafine kaolin, herein "Kaolin A" and a fine rhombohedral PCC, herein "PCC A" with a low ratio, i.e. 40:60, of the amount by weight of kaolin to the amount by weight of calcium carbonate in the composition.

Kaolin A has the following properties:

- 10 i) GE brightness: 90.9;
 - ii) Specific surface area: 23 meters squared per gram;
 - iii) Shape factor: 8;
 - iv) Median particle size: 0.18 microns;
- Particle size properties (x and P as defined 15 v) earlier):

	X (micron)	P (%)
	2	99
20	1	99
	0.5	94
	0.25	69

PCC A has the following properties:

- 25 (i) GE brightness: 95
 - Median particle size: 0.5 microns; (ii)
 - (iii) Particle size properties (x and P defined earlier):

30	X	(microns)	P (%)	_
	2		.78	_
	1		92	

0.5	48
0.25	12

A coating composition was made using the pigment 5 composition together with water and a binder system. The coating composition contained as a binder system 16% by weight, on an active basis, of a styrene acrylic copolymer latex, based on the dry weight of the minerals and 1.5% by weight, on an active basis, of Protein 10 Technologies Procote 2500 protein, based on the dry weight of the pigments present. The composition also contained 0.5% by weight, on an active basis, based on the dry weight of the minerals of Nopcote C-104, a calcium stearate lubricant and 0.1% by weight, on an 15 active basis, based on the dry weight of the pigments of a sodium polyacrylate dispersant.

The coating composition was made down, i.e. formed into an aqueous suspension, at a target pH of 8,5 - 9.0 at a solids concentration which was the highest able to 20 give the suspension an acceptable runnability, measured as a Brookfield viscosity of from 2500 to 3000mPa.s at 20rpm and a temperature of 22C.

The coating composition was applied to a pre-coated SBS base sheet of North American origin using a 25 laboratory coating machine. The coating composition was applied to a surface of the base sheet so as to give a target coat weight of 12g.m⁻². The coater speed was kept constant at 400m.minute⁻¹ (6.7m.s⁻¹). The coated sheet produced was calendered using a Beloit 750 lab calendar 30 using the calendering conditions of 150°F (66°C), 300 PLI

WO 00/66509

(pounds per linear inch) (5200kg.m⁻¹), 25 fpm (feet per minute) (0.13m.s^{-1}) , and 2 nips.

-22-

PCT/US00/10824

The coated, calendered sheets were then tested for physical and optical properties using standard testing 5 procedures.

The sheet and print gloss were measured using a laser goniophotometer. In this type of measurement a laser beam is reflected off a surface and the angular intensity distribution of the specularly reflected light 10 is measured. The measurement device uses a red HeNe laser with a wavelength of 632.8nm and a beam diameter of 0.8mm. The beam was used at an incidence angle of 75 degrees from the surface normal for direct comparison to The ISO sheet 75 degree TAPPI gloss measurements. 15 brightness, or percentage reflectance to violet light of the coated paper, was measured in a manner well known to those skilled in the art using a Technidyne Micro TB-1C brightness meter.

The results are shown in Table 1 later.

20 EXAMPLE 2

A pigment composition embodying the invention was prepared using Kaolin A as in Example 1 and a fine aragonite PCC, herein "PCC B" with a low ratio of the amount of kaolin to the amount of calcium carbonate in 25 the composition.

PCC B employed in this composition has the following properties:

- (i) GE brightness: 93
- (ii) Median particle size 0.34 microns;

-23-

PCT/US00/10824

	Х	(microns)	P	(왕)
5	2		96	5
	1		83	3
	0	. 5	67	7
	0	. 25	28	3

A coating composition was prepared in the same manner as described in Example 1 using this pigment composition. The coating composition resulting was calendered and applied to a base sheet as used in Example 1 in the manner described in Example 1 and the properties 15 of the coated sheet were measured as in Example 1.

The results are given in Table 1 later.

EXAMPLE 3

As a comparative example, a pigment composition was prepared as in Example 1 except that the composition was 20 formed as a blend of another kaolin, 'Kaolin B' and a ground clacium carbonate 'GCC A' in a weight ratio of 60 parts Kaolin B to 40 parts GCC A.

Kaolin A has a GE brightness of 90.8 and a median particle size of 0.45 microns. GCC A has a GE brightness 25 of 97 and a median particle size of 0.7 microns.

A coating composition using this bigment composition was prepared as described in Example 1 and sheets using this coating composition were prepared and their properties measured as in Example 1. The results are 30 shown in Table 1 as follows.

TABLE 1

	Example	1	2	3
		(invention)	(invention)	(comp.)
	ISO sheet	81.2	81.3	80.8
	brightness			
	75 degrees	70.2	72.6	60.1
5	TÀPPI			
	Sheet gloss			

As seen in Table 1 the compositions of the invention unexpectedly give a superior combination of sheet 10 brightness and gloss.

EXAMPLE 4

A further coating composition embodying the invention was made in the manner described in Example 1 using as pigment composition, 'P4A', a blend of Kaolin A 15 and PCC B, both as described earlier, in a weight ratio of 25:75 (kaolin:PCC). The ISO brightness and sheet gloss of paper sheets coated as in Example 1 were measured as described in that Example.

For comparison purposes, the experiment was repeated 20 except that a commercially available ground calcium carbonate 'GCC B' was used in place of PCC B in a pigment composition P4B.

GCC B has the following properties:

- (i) a GE brightness of 95;
- 25 (ii) a median particle size of 0.42 microns; The results obtained are given in Table 2 as follows.

TABLE 2

Pigment	Sheet	Sheet gloss at	
composition	brightness	75 degrees	
	(ISO)		
P4A (invention)	82.1	71	

-25-

P4B	81.3	68
(comparative)		

As seen in Table 2, both sheet brightness and sheet gloss 5 are beneficially improved by use of the pigment composition embodying the invention, P4A. This is surprising, since the carbonate used in the comparative pigment composition P4B has a higher powder brightness than that used in composition P4A embodying the 10 invention.

The BET surface areas of each of pigment compositions P4A and P4B were measured. Compositions P4A and P4B were found respectively to have specific surface areas of 16 and 20 meters squared per gram. Beneficially, 15 Composition P4A was found to have, in consequence, a reduced binder demand in a coating composition.

CLAIMS

We claim:

- 1. A pigment composition for use in coating a paper product, comprising a blend of at least two particulate 5 inorganic materials comprising (a) a high brightness ultrafine kaolin produced from a blocky kaolin clay, the kaolin having a median particle size less than about 0.5 microns (μ m) and (b) a fine coating precipitated calcium carbonate (PCC) having a median particle size less than 10 about 0.8 microns, the ratio by weight of the PCC to the kaolin being greater than 1.0.
 - 2. The pigment composition of claim 1 wherein at least 50% of said PCC has an aragonite crystal morphology.

15

- 3. The pigment composition of claim 1 wherein at least 50% of said PCC has a rhombohedral crystal morphology.
- 4. The pigment composition of claim 1 wherein said 20 kaolin has a median particle size of between about 0.1 and about 0.3 microns and said PCC has a median particle size of less than about 0.55 microns.
- 5. The pigment composition of claim 2 wherein said PCC 25 has a median particle size of between about 0.25 and about 0.45 microns.
- 6. The pigment composition of claim 3 wherein said PCC has a median particle size of between about 0.35 and 30 about 0.55 microns.

WO 00/66509

-27-

PCT/US00/10824

- 7. The pigment composition of claim 1 wherein said kaolin comprises greater than 55% by weight of particles having a particle size of less than 0.25 microns.
- 58. The pigment composition of claim 1 wherein said kaolin has a particle shape factor of 15 or less.
- 9. The pigment composition of claim 1 wherein the percentage by weight of said kaolin in said pigment 10 composition is in the range from about 10% to about 45% by weight and the percentage by weight of said PCC in said pigment composition is in the range from between about 55% to about 90%.
- 1510. A paper product coating composition comprising an aqueous suspension of the pigment composition of claim 1 and a binder.
- 11. The coating composition of claim 10 wherein said 20 coating composition contains a pigment dispersant.
 - 12. The coating composition of claim 10 wherein said coating formulation contains a lubricant.
- 25 13. A method for coating a paper product by applying the coating composition of claim 10 to coat a surface of the paper product.
- 14. The method of claim 13 wherein said paper product is 30 a solid bleached sulfite paper product.

-28-

15. A method of improving the optical and printing properties of a paper product, comprising adding the pigment composition of claim 1 to an aqueous suspension comprising a binder to form a runnable coating 5 composition and applying said coating composition to at least one surface of said paper product.

16. The method of claim 16 wherein said paper product is a solid bleached sulfite paper product.

10

INTERNATIONAL SEARCH REPORT

International application No. PCT/US00/10824

A. CLASSIFICATION OF SUBJECT MATTER							
IPC(7) :C04B 14/02, 14/10, 14/28; C09C 1/02, 1/42 US CL :106/416, 464, 468, 486, 487; 162/181.1, 181.8							
According to International Patent Classification (IPC) or to both national classification and IPC							
B. FIELDS SEARCHED							
Minimum documentation searched (classification system followed by classification symbols)							
U.S. : 106/416, 464, 468, 486, 487; 162/181.1, 181.8 IPC(7): 14/02, 14/10, 14/28; C09C 1/02, 1/42							
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE							
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) NONE							
C. DOC	UMENTS CONSIDERED TO BE RELEVANT						
Category*	Citation of document, with indication, where app	ropriate, of the relevant passages	Relevant to claim No.				
Y	US 5,833,747 A (BLEAKLEY ET (10/11/98), see column 1, line 3-column	1-16					
Y	US 5,478,388 A (GANE ET AL.) 26 see column 3, line 33-column 6, line 6	1-16					
Y,E	US 6,074,474 A (BROOME ET AL.) 1 column 3, lines 40-56 and the claims.	1-9					
Y	US 5,879,512 A (McGENITY ET AL.) see column 1, line 65-column 2, line 8	12					
Y	US 5,749,958 A (BEHL ET AL.) 12 N claims.	1,4,7,8					
X Further documents are listed in the continuation of Box C. See patent family annex.							
* Sp	ernational filing date or priority ation but cited to understand the ention						
"E" ca	Considered novel of Cannot be Const						
cited to establish the publication date of another citation or other special reason (as specified)		"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is					
"P" do	ocument referring to an oral disclosure, use, exhibition or other means becument published prior to the international filing date but later than e priority date claimed	combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family					
Date of the actual completion of the international search Date of mailing of the international search report							
21 JUNE 2000 14 AUG 2000							
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Workington D.C. 20221		Authorized officer MICHAEL MARCHESCHI	DEBORAH THOMAS AND PARALEGAL SPECIALIST				
Washington, D.C. 20231		Telephone No. (703) 308-0661					

Form PCT/ISA/210 (second sheet) (July 1998)*

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

□ BLACK BORDERS
□ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
□ FADED TEXT OR DRAWING
□ BLURRED OR ILLEGIBLE TEXT OR DRAWING
□ SKEWED/SLANTED IMAGES
□ COLOR OR BLACK AND WHITE PHOTOGRAPHS
□ GRAY SCALE DOCUMENTS
□ LINES OR MARKS ON ORIGINAL DOCUMENT
□ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

IMAGES ARE BEST AVAILABLE COPY.

OTHER:

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.